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Ultra-refractory diboride ceramics for solar plant receivers

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Abstract

Concentrating Solar Power (CSP) is considered to be one of the most promising and sustainable technologies for electricity production in the future, and as efficiency of solar thermal systems rapidly increases with increasing working temperature, the big challenge for future is to develop novel solutions for solar receivers. In this framework, Ultra-High Temperature Ceramics (UHTCs) are mainly studied as thermal protection materials for aerospace and military applications, but their peculiar properties (very high melting points and good thermo-mechanical properties at high temperatures) can be advantageously exploited to increase the operating temperature of thermodynamic solar plants in concentrating solar power systems. This work is devoted to the study and characterization of the spectral reflectance of hafnium and zirconium diborides containing MoSi₂ as secondary phase in order to evaluate their potential as novel solar absorbers. To assess the spectral selectivity properties, room-temperature hemispherical reflectance spectra were measured from the UV wavelength region to the mid-infrared, considering different levels of porosity for each system, in order to understand how porosity affect spectral reflectance. Moreover, for zirconium diboride and hafnium diboride composites containing 10vol% of MoSi₂ sintering aid, the thermal emittance was measured in the 1100–1400K temperature range in PROMES-CNRS solar furnace. Data obtained were compared with spectral characteristics and high temperature emittance of a monolithic silicon carbide.

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1. Introduction

A sustainable, efficient and renewable way to provide energy is the challenge that this generation has to face in order to leave long-term perspectives to next generations. For this purpose, concentrating Solar Power (CSP) is considered to be one of the most promising and sustainable technologies both for electricity [1] and solar fuels production [2-4]. For both applications, the increase of the plant operating temperature is a critical requirement for increasing the overall system efficiency. The key parameter is the absorber material constituting the solar receiver, which is devoted to collect and efficiently transfer to the thermal exchange medium the energy concentrated by the whole mirror field. The ideal sunlight absorber for high temperatures must possess a series of favourable properties: a good mechanical and chemical stability at the required high temperatures, good thermomechanical characteristics, a high sunlight absorbance and a low thermal emittance at the operating temperatures. From the optical properties point-of-view, latter requirements translate in a low reflectance (ideally approaching zero) at the solar spectrum wavelengths ($\lambda < 3 \mu\text{m}$) and a high reflectance (ideally approaching 100%) for longer wavelengths. The transition wavelength from the low to the high reflectance spectral regime changes according to the required plant operating temperature, i.e. to the thermal emission spectrum of the heated absorber [5-7]. Few materials are currently under study for tower solar receivers, mainly for the volumetric absorber scheme: alumina [8] and silicon carbide (SiC) [9]. Alumina is an oxide material characterized by very high thermal stability, oxidation resistance and high refractoriness, but, being white, with non-optimal sunlight absorption. SiC is a non-oxide grey semiconductor with good sunlight absorption and high oxidation resistance, but also with a high thermal emittance.

Diborides of transition metals such as ZrB_2 , HfB_2 are commonly referred to as ultra-high temperature ceramics (UHTCs) for their extremely high melting temperatures exceeding 3000 °C, solid-state stability, good thermochemical and thermo-mechanical properties, high hardness, high electrical and thermal conductivities [10-12]. UHTCs are ideal for thermal protection systems, especially those requiring chemical and structural stability at extremely high operating temperatures. Up to now, UHTCs are mainly employed in the aerospace industry for hypersonic vehicles, rocket motor nozzles or atmospheric entry probes capable of the most extreme entry conditions [10-12].

In the framework of CSP thermodynamic sunlight exploitation, the ultra-high melting point of UHTCs, together with the unique combination of good thermal conductivity and chemical stability appear intriguing for employing them in high temperature novel solar furnaces, mainly as volumetric absorbers as a possible alternative to materials used up to now. In this framework the study of both bulk and porous material is important to investigate the possibility of their use in a foam shape. To assess the potential of UHTCs as selective sunlight absorber in solar furnaces devoted to work in the high temperature regime, the spectral absorber properties of these materials need to be evaluated. Studies of spectral emittance characteristics of either bulk [13-16] or film samples [17] of UHTCs dated back to the 60–70 s and were conducted in the framework of space or military applications. Due to the intrinsic difficulty to perform high temperature emittance measurements and to the fact that emittance strongly depends on the particular material composition, fabrication method [16] and surface finishing [13-16], available literature data, if any, are also difficult to interpret and to compare. For example, they show different emittances for materials produced by different suppliers while not giving information about several important parameters such as actual material composition, densification level, surface finishing, porosity etc. In addition, available data often refer to different physical quantities (total hemispherical, total normal or spectral normal emittances) or disagree among each other. Very recently we characterized the room temperature spectral reflectance and high temperature total emittance properties of some UHTC carbides [18-20], while, to the best of our knowledge, reports on the optical properties of ceramic diboride materials and focused on their application for solar energy exploitation are lacking. In the present work we describe the comparative optical characterization of various zirconium and hafnium diborides, with different density levels. We measured the room-temperature hemispherical reflectance spectra from the ultraviolet (UV) to the mid-infrared (MIR) wavelength regions. In particular, UV–visible–near infrared (NIR) spectra allowed us to characterize the sunlight absorbing properties of the samples, whereas investigations in the MIR region allowed a preliminary evaluation of the material properties for use as high-temperature thermal emitter. Moreover, for selected ZrB_2 and HfB_2 samples, we measured the total hemispherical emittance in the wavelength range from 0.6 to 40 μm for temperatures ranging from 1100 to 1400K in vacuum. In fact a possible drawback of such materials could be oxidation phenomena expected to occur when composites are exposed to air at higher

temperatures. This aspect will be subject of further work, and this possibility could be relaxed if the absorber operates in vacuum or, more likely, under inertial atmosphere. For a more significant assessment of actual UHTC potential as solar absorber, the optical properties of UHTC samples are compared with those of a sample of monolithic SiC.

2. Methods

2.1. Materials preparation and characterization

Commercial powders were used to prepare the ceramic materials. Compositional details are reported in Table 1. ZrB₂ and HfB₂-based materials were either pure samples or prepared with MoSi₂ as sintering aid, with a typical content of 5–10vol%.

Samples constituted by monolithic SiC were also produced. After sintering, flat surfaces were prepared by grinding and polishing the sintered materials with diamond pastes up to 1 μ m. The mean surface roughness (R_a) was measured according to the European standard CEN624-4 using a commercial contact stylus instrument (Taylor Hobson mod. Talysurf Plus) fitted with a 2 μ m radius conical diamond tip over a track length of 8 mm and with a cut-off length of 0.8 mm. Surface roughness values for the polished samples are reported in Table 1. Microstructural features were analysed by scanning electron microscopy (SEM, CambridgeS360, Cambridge, UK) and energy-dispersive spectroscopy (EDS, INCA Energy 300, Oxford Instruments, High Wycombe, UK) and image analysis (Image pro plus 7.0).

The samples selected for high temperature emittance measurements were prepared in discs of 40 mm diameter, 2 mm thickness and 300–400 nm surface roughness. In order to make a comparison with materials used as solar absorber, SiC discs were also prepared with 300 nm surface finishing.

Table 1. Compositional details of UHTCs for reflectance spectra.

Matrix	Sample label	Density (%)	Sintering additive amount (vol%)	Mean pore diameter (μ m)	Min-max pore diameter (μ m)	Surface roughness R_a (μ m)
ZrB ₂	ZB75	75	0	3.5	0.5 – 11	~0.05
ZrB ₂	ZB85	85	5	2.3	0.5 – 9	~0.05
ZrB ₂	ZB95	95	10	1.5	0.4 – 4	~0.03
ZrB ₂	ZB97	97	10	0.4	0.1 – 4	~0.04
HfB ₂	HB75	75	-	1.8	0.5 – 8	~0.03
HfB ₂	HB85	85	3	0.9	0.5 – 4	~0.05
HfB ₂	HB95	95	5	1.9	0.7 – 8	~0.03
HfB ₂	HB99	99	5	<0.1	-	~0.02

2.2. Reflectance spectra (room temperature)

Optical reflectance spectra in the 0.25–2.5 μ m wavelength region were acquired using a double beam spectrophotometer (Lambda900 by PerkinElmer) equipped with a 150 mm diameter integration sphere for the measurement of the hemispherical reflectance. The spectra in the wavelength region 2.5–14.3 μ m have been acquired using a Fourier Transform spectrophotometer (FT-IR “Excalibur” by Bio-Rad) equipped with a gold-coated integrating sphere and a liquid nitrogen-cooled detector. In all cases the reflectance spectra are acquired for quasi-normal incidence.

2.3. High temperature emittance

Hemispherical emittance at high-temperature has been measured using the MEDIASE setup (Moyen d’Essai et de Diagnostic en Ambiance Spatiale Extreme) of the PROMES-CNRS Megawatt Solar Furnace. MEDIASE is

composed by a vacuum chamber with ultimate pressure limit of 10^{-6} mbar, equipped with a hemispherical silica glass window of 35 cm diameter. Fig. 1 shows the scheme of the experimental chamber, that can be equipped with various additional instruments if required by the experiment. The water-cooled sample holder is set to keep the specimen at the focus of the 1-MW solar furnace. Care was taken in mounting the sample in such a way to minimize the thermal losses towards the holder. The directional radiance was measured on the rear face of the sample at different angles thanks to a movable, computer-controlled three-mirror system. The light detector was a radiometer sensitive to the 0.6–40 μm wavelength range. The radiance was collected from a small region of about 7 mm diameter (for 0° angle of incidence) around the center of the sample using a Cassegrain optical system in front of the radiometer. The spectral response of the optical system was calibrated against a reference blackbody.

At given angle θ and temperature T , the directional emittance $\varepsilon(\theta, T)$, integrated on the sensitivity range of the detector, was obtained as the ratio between the measured radiance $I(\theta, T)$ and the blackbody directional radiance $I_B(T)$. Hemispherical emittance values $\varepsilon^h(T)$ were calculated by integration of the angular values over a half space, assuming hemispherical symmetry of the emission lobe. The surface temperature was read near the center of the sample to minimize border effects, using a pyro-reflectometer specifically developed at PROMES-CNRS [21, 22] and approximated by the color temperature [23]. The relative standard uncertainties of the temperature measurement are typically from 0.5 to 1%, while the relative standard uncertainty of the emittance measurement is 2.5%.

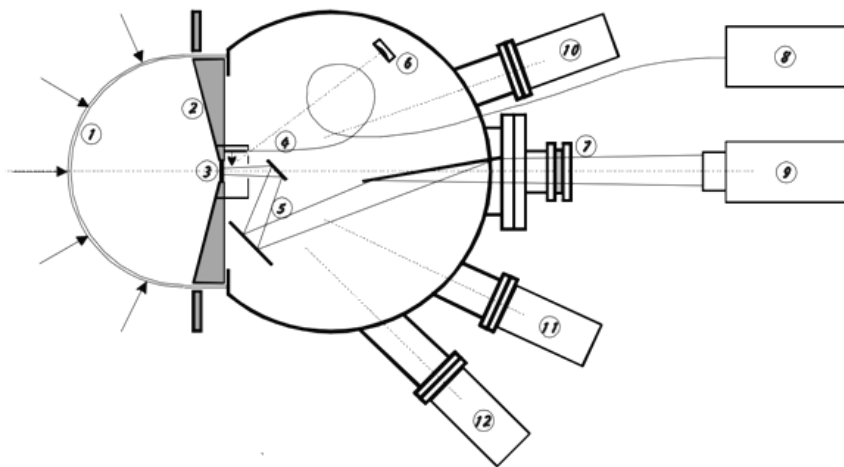


Fig. 1: Scheme of the MEDIASE setup. 1) hemispherical window; 2) water-cooled thermal shield and sample holder; 3) specimen; 4) optical fiber; 5) 3-mirror goniometer; 7) measurement window; 8) bichromatic pyro-reflectometer; 9) radiometer and 6), 10), 11), 12) holders for additional instruments (none for experiment here described).

3. Results

3.1. Microstructural properties of diboride samples

In Fig. 3 the microstructural details of the samples under investigation are illustrated. In order to obtain fully dense diborides, at least an amount of 5–10 vol% of MoSi_2 and a temperature of 1850 $^\circ\text{C}$ are needed. When lower amount of MoSi_2 and/or lower temperature are used, samples with residual porosity are achieved. As example, ZrB_2 without sintering aids resulted in samples with 25% (ZB75) porosity as confirmed by both density and porosity evaluation. The density was raised to 85% (with a sintering temperature of 1800 $^\circ\text{C}$) by adding just a 5 vol% of MoSi_2 . At last, increasing both the sintering temperature to 1850 $^\circ\text{C}$ and the MoSi_2 content to 10%, the final relative density reached 95–97%. Morphology and pore shape is shown in the micrograph of Fig. 3 while pore diameter frequency distribution is illustrated in Fig. 2. Frequency distribution shows that in dense samples, the peak is about 0.5–1.5 μm , while in porous ones, the pore diameter are comprised in the range 0.5–8 μm . Comparing ZrB_2 and HfB_2 at fixed porosity, HfB_2 samples tend to have larger pores.

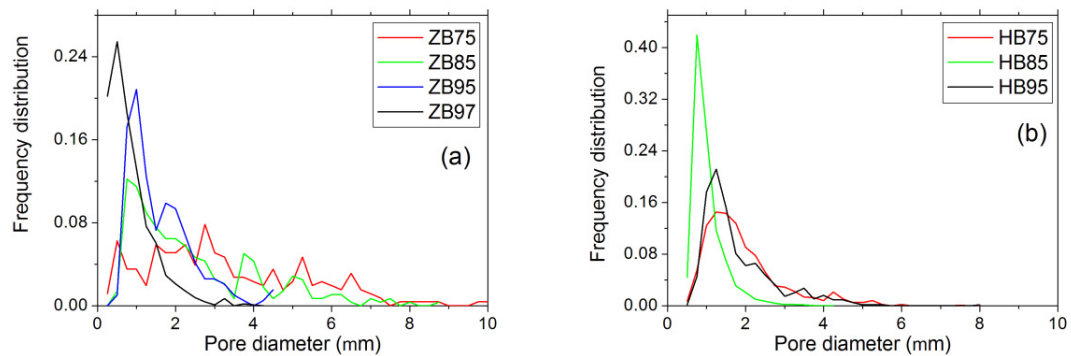


Figure 2. Pore diameter distributions: ZrB₂-based materials (a, left) and HfB₂-based materials (b, right).

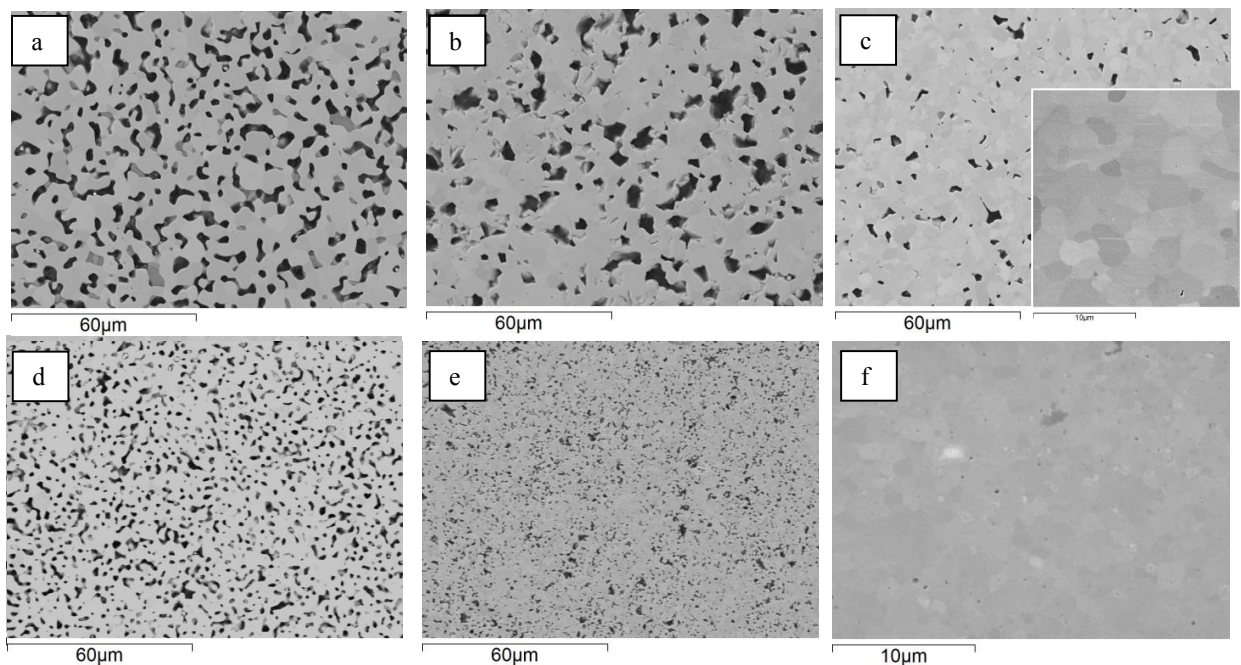


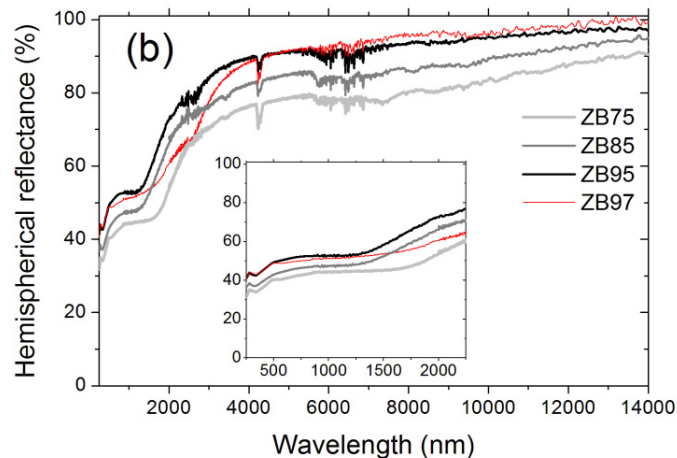
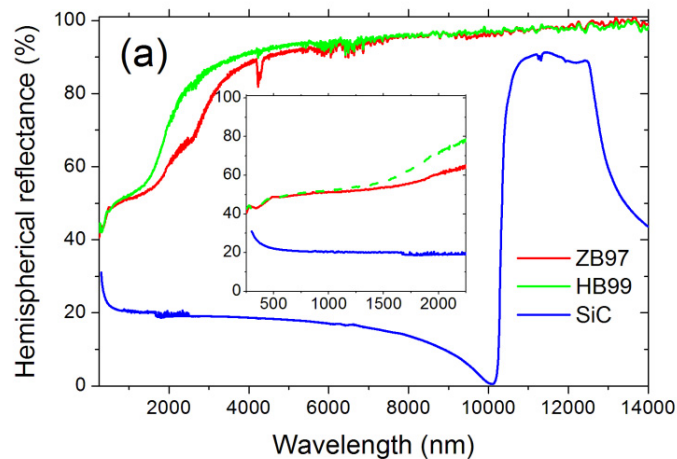
Figure 3. Microstructural features of borides. Pore amount and morphology in a) ZB75, b) ZB85, c) ZB95. Inset in fig 2c represents the typical microstructure of ZrB₂-MoSi₂ composites. Pore amount and morphology in d) HB75, e) HB85. f) Typical microstructure of HB99.

3.2. Reflectance spectra (room temperature)

The hemispherical reflectance spectra at room-temperature are shown in Figure 4, a-c. Is shown also, in the inset the detail of the 0.3-2.5 μm wavelength range. Figure 4a compares the reflectance curves of dense ZrB₂ and HfB₂ materials with that of SiC. Reflectance curves of borides are very similar each other and with a step-like behavior, characterized by low reflectance values in UV-VIS and high reflectance values in the MIR. On the contrary, Silicon Carbide shows the typical spectrum of a semiconductor, with a well defined reststrahlen band at around 12 μm and a considerably lower value of the reflectance for longer infrared wavelengths. Figure 4-b shows the reflectance spectra of zirconium diborides for compositions with different densities. It can be appreciated a gradual increase of

reflectance with increasing density, due to the decrease of light trapping by the material pores with increasing sample density. When the density reaches 90-95% there is no appreciable difference amongst the samples.

Concerning Hafnium-based diborides, from the spectra in Fig. 4c they can be divided in two groups, according to their reflectance values for wavelengths shorter than about 10 μm . Samples with densities in the range 75-85% have a lower reflectance, with almost no spectral differences among them, while samples with higher densities show higher reflectance curves very similar each other in the wavelength range 3-10 μm , with some differences in the range 1-3 μm that can be reasonably ascribed to light trapping within residual surface pores. For wavelengths longer than 10 μm the reflectance curves of all samples converge to a value higher than 95%, which increases with the wavelength. Similarly to ZrB_2 samples, a secondary reflectance minimum at wavelengths slightly shorter than 2 μm was detected in all the HfB_2 spectra. Finally, it should be noticed that the reflectance spectra of zirconium diboride-based samples show quite scattered curves with respect to the hafnium-based ones, that displays a more defined step-like behavior. This could be probably ascribed to the higher pore size dispersion described in Sect. 3.1.



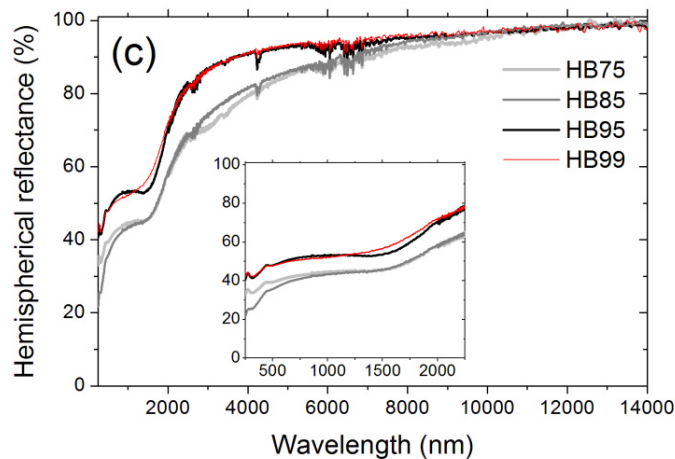


Fig.4. Reflectance curves: a) dense ZrB_2 , HfB_2 and SiC samples; b) ZrB_2 samples with different level of porosity; c) HfB_2 samples with different level of porosity

3.3. High temperature emittance

Samples for high temperature emittance characterization are indicated with an asterisk as it indicates a different surface finishing with respect to the samples used for room-temperature reflectance measurements. Specifically, ZB97* has a mean surface roughness of $0.3 \mu\text{m}$ and HB99* of $0.4 \mu\text{m}$. Fig. 5 shows the measured temperature-dependent hemispherical emittance of ZB97* and HB99*. The obtained data are compared with a sample of a 90% dense silicon carbide with $0.3 \mu\text{m}$ surface roughness. Both borides show similar high-temperature emittance values, in agreement with the similarity of their room-temperature spectral reflectance curves. On the other hand, from Fig. 5 we can appreciate that emittance of borides is significantly lower of that of silicon carbide (about a half of it in the temperature range 1300-1400 K).

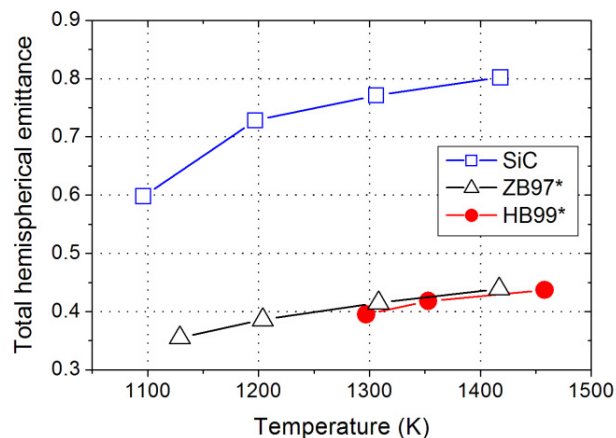


Figure 5. Comparison of the measured total hemispherical emittance of Zirconium and Hafnium diborides and Silicon Carbide as a function of the temperature.

4. Discussion

The ideal solar absorber, as already said, has to be spectrally selective against the thermal radiation with a low reflectance (ideally approaching zero) at the solar spectrum wavelengths and a high reflectance (ideally approaching 100%) for longer wavelengths. A low radiative emission at the operating temperature is required to minimize energy losses and to avoid heating of elements surrounding the absorber. In fact, energy losses via thermal emission significantly affect the overall system efficiency. Moreover, as thermal emittance increases with the temperature, a large emittance value negatively affects also the wished increase of the operating temperature for the thermodynamic solar plant. Furthermore, for the practical use, the absorber melting point should be far higher than operative temperatures. The material should possess mechanical resistance up to the operative temperatures and critical thermal shock resistance compatible with the concentrated solar radiation to face possible operating temperature variations (caused, for example, by variations of weather condition, clouds, etc). Finally, a high thermal conductivity is desired because the absorber should efficiently transfer the collected heat to a thermo-convective fluid. In this respect, borides seem to accomplish all these requirements. In fact the optical behavior of the investigated borides can be clearly recognized by step-like reflectance curves with low reflectance in the UV-VIS and high reflectance values in the medium infrared. In addition the emittance of ZrB_2 and HfB_2 in the investigated temperature range is very low. Also, thermo-mechanical requirements are satisfied: for borides, typical values of mechanical strength at room temperature range from 500 to 800 MPa, depending on the sintering procedure [24-27]. At 1773 K, specifically for composites containing MoSi_2 in suitable amounts (10-20vol%), flexural strength can reach 650 MPa and 550 MPa in air for zirconium and hafnium diborides respectively [24]. Regarding thermal conductivity, according to recent results in the literature, it is 56 W(m K)^{-1} for monolithic ZrB_2 at room temperature and increases gradually to 67 W (m K)^{-1} up to at 1675 K [28]. For HfB_2 values as high as 104 W(m K)^{-1} were reported [10]. Regarding chemical stability, conditions adopted for high temperature characterization are very mild, both for the chosen temperatures and for the high level of vacuum (10^{-6} mbar). On the contrary, in the case that ZrB_2 or HfB_2 composites are exposed to air at higher temperatures, oxidation phenomena are expected to occur. For the specific case of $\text{ZrB}_2\text{-MoSi}_2$, oxidation involves formation of an external amorphous borosilicate layer resulting from oxidation of MoSi_2 , producing silica, and ZrB_2 , producing boron oxide, when the temperature is higher than 1450 K [29]. As emittance of silica is as high as 0.8, it is expected that oxidation phenomena can significantly raise the emittance of the absorber, thus the oxidation behavior of borides will be the subject of further investigations. However, this possible drawback could be relaxed if the absorber could be operated in vacuum or, more likely, under inertial atmosphere.

The indication obtained by experimental data is that either the total amount of porosity and the pore size affects the reflectance of borides. ZB75 and ZB85 are characterized by pores and cavities as large as 10-15 μm . Due to this, they are able to partially trap radiation and their reflectance values are always lower than those of ZB95 and ZB97 in the overall range of investigated wavelengths.

On the other hand, porous HfB_2 samples (namely HB75 and HB85), show reflectance values which are similar to those of dense samples for $\lambda > 8\text{-}10 \mu\text{m}$, due to the fact that pores are much smaller than those of ZrB_2 porous samples with similar levels of porosity. Thus, in this class of materials, a difference in reflectance are only seen in the range 0-8 μm . It is worthy to note that in HB95 pore dimension range is similar to HB75. Nevertheless, its reflectance is closer to that of a fully dense material such as HB99. In this case, reflectance values suggest that total amount of pores rather than their dimensions dictates the reflectance values. Although borides show the mentioned step like reflectance behavior, room temperature reflectance values are still quite high in the sunlight spectral range. One way to improve the ability of the material to absorb the solar radiation is tailoring the material porosity to efficiently capture the radiation. Data obtained so far showed that the porosity obtained by leaving an incomplete material sintering are partially effective in improving the material absorbance.

SiC has been recently started to be employed as absorber in solar applications. In spite of that, very few information is available in the literature on its optical properties, especially at high temperature. The room temperature optical spectrum of SiC shows, differently from borides, the typical shape of semiconductor materials with a well defined absorption band. Furthermore, SiC has a much higher absorbance at solar spectrum wavelengths when compared to borides.

In the high temperature regime, the major differences between borides and SiC are displayed in all the investigated

temperature range (1100–1450 K); in fact the emittance of SiC is significantly higher than that of the tested boride-MoSi₂ composites.

5. Conclusions

In the present paper we evaluated the intrinsic spectral selectivity of different Ultra High Temperature Ceramics, hafnium and zirconium diborides, to evaluate their potential for novel sunlight absorbers in tower solar plants operating at higher temperature. Room-temperature hemispherical reflectance spectra from 0.25 to 14 μm , were measured, evidencing typical curves with a low reflectance in the UV-VIS-NIR wavelength region and a high reflectance plateau at the wavelengths of the thermal infrared. We evidenced favorable spectral characteristics of borides over SiC, that reasonably arise in a higher absorbance over emittance ratio and thus in superior solar absorber performances. Within the boride family, hafnium and zirconium boride are expected to show similar performances. In general, dense samples appear more promising than porous ones. Moreover, for samples of dense zirconium and hafnium boride, we measured the high-temperature hemispherical emittance integrated in the wavelength range 0.6–40 μm , obtaining an emittance value around 0.4 for temperatures from 1100 to 1450 K. Both room-temperature reflectance spectra and high-temperature emittance very favorably compare UHTC borides against SiC, thus proposing UHTC borides as good candidates for novel absorbers able to raise the operating temperature of thermodynamic solar plants.

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